SYNTHESIS AND APPLICATIONS OF PERSISTENT LUMINESCENCE NANO-MATERIALS

SHORT SYNOPSIS

Submitted in partial fulfillment of the requirement of the degree of

DOCTOR OF PHILOSOPHY

to

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by

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ABSTRACT

Persistent luminescence is a light emission property of certain compounds which are capable of storing the electrons on trap states or defect states. The emitted light can last for few minutes to several hours, even the excitation is stopped. Therefore, the persistent luminescence materials can find their applications in signaling, emergency exits, needles/dials of watches, and toys. Such compounds can be proposed for other applications by modifying the mechanism of long persistent luminescence. Such modified materials are known as up-conversion persistent luminescence (UCPL) materials. In UCPL, the emission of shorter wavelength or higher energy is expected by applying the longer wavelength or lower energy of the excitation source. The persistent near-infrared luminescence compounds can be prepared, using the UCPL mechanism, for solid state lighting and bio-imaging. Aim of present research is to first optimize the synthesis procedure for high quality UCPL compounds and, secondly, to achieve intense emission for practical applications. We also propose to investigate the effect of size, morphology and dopants (e.g., rare earth elements) on the structural and optical characteristics of Li and Zn based UCPL compounds (e.g., $LiGa_5O_8$ and $ZnGa_2O_4$: with and without doping of rare earth elements and Cr).

Keywords: Persistent Luminescence, Synthesis, Structure and Optical properties

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1. Introduction

Solid-state lighting uses light-emitting technologies such as; incandescent bulbs and light emitting diodes (LED) (polymers or organic LEDs). LEDs are commercially available and widely used for; liquid-crystal displays, large outdoor displays, searchlights, cameras, interior and exterior lighting in aircraft, cars, buses, in flashlights etc. The solid-state lighting technology is highly energy efficient and has incredible potential for saving energy and reducing carbon emission. Additionally, it has many controllable properties like; range of emission spectrum, direction, color, modulation and temperature.

In continuation to the developments of solid-state lightening technologies, there are efforts to prepare electronic structure rich compounds which can emit radiation of sufficient intensity after gaining the energy from sun light. The photo-excitation process involves directing the sun light into samples, where it is absorbed and spreads excess energy into the materials. Through luminescence, the sample can dissipate the excess energy. This process is known as conventional luminescence and several phosphors have been developed in last decade [1-5].

A new type of luminescence called; up-converted persistent luminescence (UCPL) process has been designed by combining the features of; up-conversion and long-persistent luminescence properties [6-10]. The up-conversion luminescence (UCL) works by converting low-energy excitation into high-energy emission, usually at near-infrared wavelengths to visible wavelengths [11-15]. Under the excitation of low frequency or longer wave-length of light photons, the ionic system moves from the ground state (G) to a higher-energy excited state via an intermediate metastable state (M). After nonradiative relaxation, the excited ion from the emitting state (E) directly returns to the state G, accompanied by light emission with a higher energy than that of the excitation light. The left side of Fig. 1 explains the UCL process. Trivalent lanthanide ions such

as Ln^{3+}, Er^{3+}, Tm^{3+} or Ho^{3+} are commonly used, for creating metastable energy states, in conventional UCL materials because of their ladderlike arranged energy levels, which promote the absorption and transfer of photons [11-15].

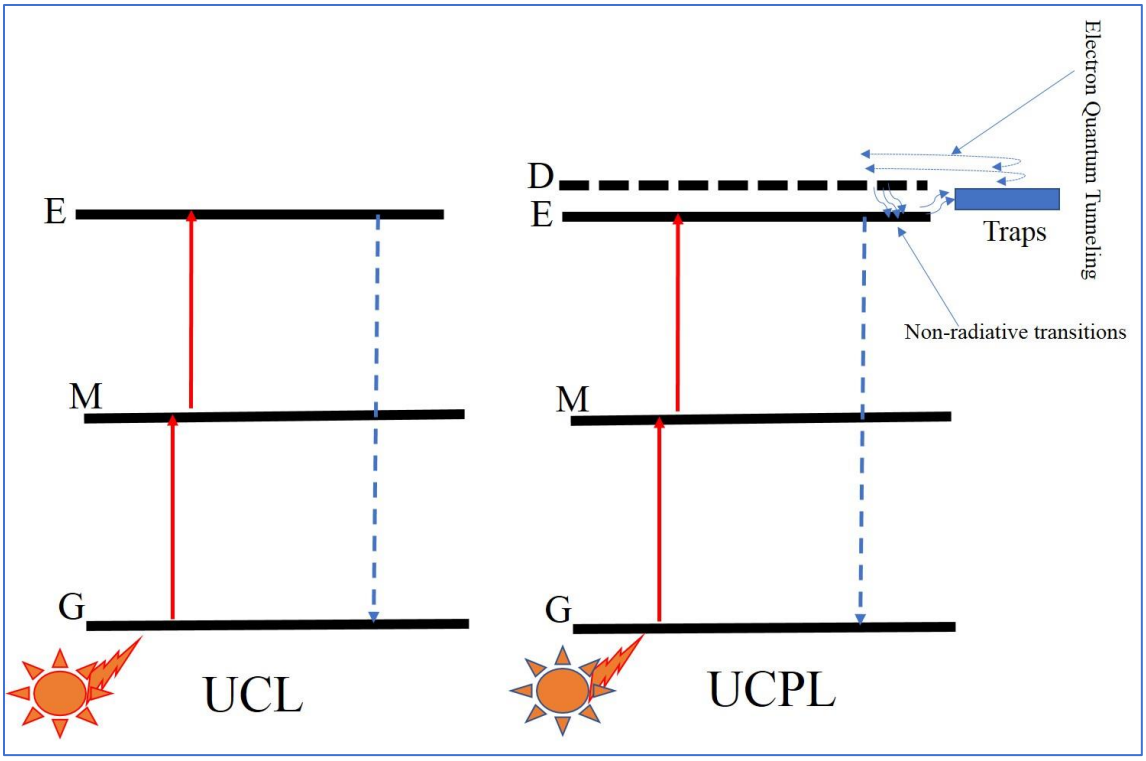

Fig 1. Schematic diagram of up-conversion luminescence (UCL) and up-converted persistent luminescence (UCPL).

On the other hand, once the UCL process is completed, electrons are reached at excited states (E) and a delocalized state (D; a typical higher energy state with delocalization characteristics). The D states are close to E energy states and formed by the empty or partly filled *d/f* electronic shells of rare earth elements. The electrons at D states may be captured/stored on the trap states. The trap states are formed by the lattice defects or neutral impurities in some of the complex compounds [16-20]. The traps can hold the electrons for long time (may be; for few seconds to several hours) before they move to the E state via electron quantum tunneling effects. The radiative emission,

with high energy compared to the incident photon energy, takes place and last for long time and depends on the storage capacity of trap states. The remarkable feature of UCPL mechanism is that the high energy persistent emission can be generated by lower excitation energy.

This phenomenon opened an avenue for the development of several complex oxide compounds which can emit light for a long time once they received pumping from sun light or NIR light sources [16-20]. The UCPL phenomena can help the scientific and non-scientific societies by developing UPCL compounds which can gain energy in the day time (by keeping them into sun light) and emit the light energy in the dark/night hours, provided that they can emit sufficient intensity. The UPCL materials may not require any electricity for their operation and will solve the energy problem (at least for the lighting need of society). A few compounds have been recently developed for exhibiting the UPCL phenomena [16-20]. However, their synthesis protocols are typical and the UPCL property is subjected to the doping element type, concentration and operation temperatures [16-20]. Aim of present research is to first optimize the synthesis procedure for quality UCPL compounds and, secondly, to achieve high intense emission for practical applications. We also propose to investigate the effect of size, morphology and dopants (e.g., rare earth elements) on the structural and optical characteristics of Li and Zn based UCPL compounds (e.g., $LiGa_5O_8$ and $ZnGa_2O_4$: with and without doping of rare earth elements and Cr). In the following section a systematic review of literature is provided which indicate the technical issues and application aspects in the development of UCPL compounds.

2. Literature Review

Yan *et al.* (2010) [11], have prepared $La_3Ga_5GeO_{14}$ compound with Cr^{3+}, Zn^{2+} dopants using solid-state reaction method. The NIR phosphorescence could be achieved under UV light irradiation (~240−360 nm). But NIR phosphorescence was barely achieved by blue light (~480nm) irradiation. The $La_3Ga_5GeO_{14}$ compound was applied in bioimaging.

Pan *et al.* (2011) [12], have prepared $Zn_3Ga_2Ge_2O_{10}$ compounds with Cr^{3+} doping using the solid-state reaction method. Cr^{3+} doped zinc-gallo-germanates, which emit NIR persistent light, could be developed which worked under the solar radiation (under various environmental conditions) and emit a long-lasting NIR afterglow (4hrs).

Liu *et al.* (2013) [14] have prepared $LiGa_5O_8:Cr^{3+}$ nano-dimensional compounds using a sol-gel and thermal annealing method. Intense emission of 716 nm light has been achieved when the $LiGa_5O_8:Cr^{3+}$ phosphor was pre-treated with ultraviolet light (250–360 nm) and then stimulated with visible light or a NIR light photons. Fig.2 shows the images of glow of compound after treatment of visible light for 120 hrs.

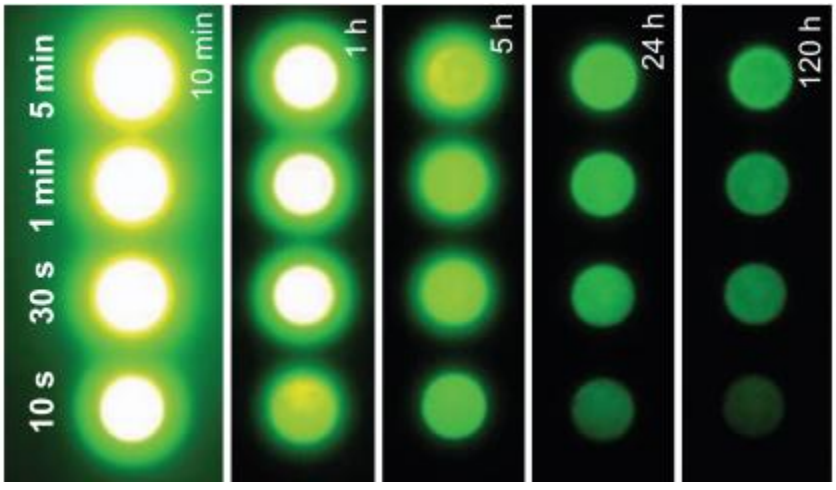

Fig.2. Emission of $LiGa_5O_8:Cr^{3+}$ phosphors for diffirent time.

B. Srivastava *et al.* (2015) [16] have prepared Cr doped $ZnGa_2O_4$ NPs with sub-ten-nanometer size using the biphasic hydrothermal route. After excitation, this smallest Cr: $ZnGa_2O_4$ nanoparticles show persistent luminescence for about one hour. This study shows the economic fabrication of UCPL compounds.

O. Q. De Clercq *et al.* (2017) [18] have prepared the $LiGa_5O_8:Cr^{3+}$ persistent phosphors which exhibit emission of NIR (> 715 nm) radiation under the visible light excitation. Doping of Si or Ge improves the persistent luminescence intensity.

Harizaj et al. (2019) [20] have prepared the $LiGa_5O_8:Cr^{3+}$ compounds using ball-milling and high temperature (1400 °C) annealing procedure. The excitation from low energy (635 nm) laser diode could produce persistent luminescence from $LiGa_5O_8:Cr^{3+}$ compound in a similar way as the persistent luminescence was produced by high energy laser irradiation (335 nm).

Xiong et al. (2021) [21] have developed the self-recoverable mechano-luminescence (ML) behavior in $LiGa_5O_8:Cr^{3+}$ which is located in the deep red wavelength range. $LiGa_5O_8:Cr^{3+}$ and $LiGa_5O_8:Cr^{3+}Al^{3+}$ powders were synthesized by a high-temperature solid-state reaction. A novel ML material with self-recoverable luminescence in a wide wavelength range, increasing the potential number of ML candidates and advancing the fundamental understanding and practical applications of ML materials.

3. Description of Broad Area and Gap Area

Based on the literature review, it is evidenced that primarily research has been conducted on the up-conversion luminescence and attempted also have been made to develop up-conversion persistent luminescence (UCPL) compounds. The lanthanide based up-conversion materials obey rich energy levels which can tune the emission characteristics of the compounds. Typical up-conversion materials consist of an oxide host matrix, with large band gap energy, ≥ 3 eV and possibility of obeying native cation/anion defects such as; interstitials, voids or grain boundaries for example; $LiGa_5O_8$, $ZnGa_2O_4$ etc,. The deep energy levels can be created by doping of rare-earth ions such as Sm^{3+}, Er^{3+}, Tm^{3+} etc. Currently, several compounds have been reported as color converters for LEDs like; orthosilicates, metal oxides, aluminates, etc. Though most of the investigated phosphors have interesting luminescence spectra, they cannot be used practically because of their low conversion efficiency. Therefore, there is need to develop new compounds (may have multi metallic elements) with enriched and tunable electronic structure properties for high efficiency and durability. Till date, not only the economic synthesis but the detailed structural/electronic structure investigations, which largely relay on the surface morphology, dopant type, and dopant concentrations, are not significantly studied the literature. Therefore, present research is aimed to; (i) optimize the synthesis procedure for quality UCPL compounds, (ii) detailed investigations for their structure and electronic structure relationship for exploring the underlying mechanism using modern techniques and, (iii) to achieve intense emission via altering the dopants and host compound elements for practical applications. We also propose to investigate the effect of size, morphology and dopants (e.g., rare earth elements) on the structural and optical characteristics of Li and Zn based UCPL compounds (e.g., $LiGa_5O_8$ and $ZnGa_2O_4$: with and without doping of rare earth elements and Cr).

4. Objectives of the Study

Following objectives are proposed in the present research work:

(i) Synthesis of undoped and doped $LiGa_5O_8$ and $ZnGa_2O_4$ nanoparticles by chemical (Hydrothermal) and bulk compounds using physical (Solid-State) synthesis methods. The new dopants like; Thulium (Tm) and Ytterbium (Yb) are planned along with the conventional dopants (Er, Ho and Sm).

(ii) Structure properties of nanoparticles will be studied using X-ray Diffraction (XRD) and Rietveld refinement analysis of XRD patterns will be carried out to study crystal structure and defects.

(iii) Light absorbance characteristics of samples will be studied with UV-Visible absorption spectroscopy.

(iv) Morphology will be studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM can also be applied for elemental detections under the energy dispersive spectroscopy (EDS) mode.

(v) The element present and electronics structure studied will be investigated using X-ray Absorption Spectroscopy (XAS).

(vi) Luminescence characteristics of samples will be analyzed using photo-luminescence spectroscopy (PL) to predict their applicability for solid state lighting (either UCL or UCPL modes).

(vii) Report the prepared compounds for practical applications in solid-state lightning and exchange of ideas/materials with existing industries.

5. Methodology to be adopted

5.1 Synthesis of undoped and doped $ZnGa_2O_4$ and $LiGa_5O_8$ phosphor material

Two different approaches are planned to prepare $ZnGa_2O_4$ and $LiGa_5O_8$ compounds namely; Hydrothermal synthesis and solid-state reaction method.

In case of Hydrothermal synthesis, chlorides/nitrides of parent elements are chosen in appropriate stoichiometry and, separately, dissolve into solvents (like; DI water or ethanol). Such solutions are mixed together under magnetic stirring and sonication (for 30 min). Then after ammonium hydroxide is used (as basic nature solution) to balance the pH (i.e., pH = 7) of above prepared mixture of solutions. Consequently, precipitation takes place. The precipitates are washed, several times, using DI water to remove biproducts of the reaction. The precipitates are heated overnight in oven (~ 100 °C) and grind using mortar-pestle. Such fine powders can be used for further testing/applications.

In case of solid-state reaction method, stoichiometric amount of oxides of constituent elements (for example; $Zn_{1-y}Ga_{2-x}Ge_xCr_yO_4$ compound is prepared using the ZnO, Ga_2O_3, GeO_2 and Cr_2O_3 powders) are crushed to form a homogeneous fine powder for pre-firing at 500 °C for 1 hrs. In the second step, the above prepared powder is again crushed and then pallets are prepared (15 mm diameter; using a 2-4 ton hydraulic press) for annealing at 850 ^{0}C in air for 4 hours. In third stage, the above prepared sample is again crushed to make fine powder and then palletized ((15 mm diameter; using a 2-4 ton hydraulic press) for sintering at 1300 ^{0}C in air for 8 hours.

5.2 Characterization and Analysis

The synthesized compounds materials will be characterized by various techniques. All these synthesis and analytical techniques are considered as research tools in material sciences. The following research tools may be used;

X-ray diffraction (XRD) study: For crystal structure and phase identification.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) study: For morphology and elemental concentration investigation.

UV-Visible absorption spectroscopy: Absorbance study and band-gap energy determination.

Photoluminescence Spectroscopy (PL) study: Luminescence properties investigations (UCL or UCPL).

X-ray Absorption Spectroscopy (XAS) study: Electronic structure study (i.e., hybridization of frontier orbitals and electronic transfer mechanism)

6. Expected Outcome of the research

In this research, we are expecting synthesis of new and high-quality light emitting compounds which will be having up-conversion long persistence luminescence (UCPL) properties. We are expecting that the structural disorders (interstitials, voids or grain boundaries) produced by dissimilar element doping can provide essential trap states to the compounds. Moreover, the empty/partly occupied density of states (i.e., d/f shells) of newly preferred elements; Thulium (Tm) and Ytterbium (Yb), along with the conventional dopants (Er, Ho and Sm) are anticipated to provide deep levels to the compounds (as meta stable states in Fig.1). Therefore, overall, we can anticipate quality UCPL compounds from this study for their potential applications in new era of solid-state lightning with superior efficiency and low cost.

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